

Trace Element Chemistry of Leonardite and
Its Potential Effect on Soil Geochemistry and Plant Growth

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Leonardite, a low BTU, naturally oxidized lignitic material has been suggested as a possible amendment for reclamation of strip mine spoils, especially orphan spoils, which are low in organic matter. These materials have a relatively high humic acid content and would be expected to improve the growth potential of these materials. It was found that in germination and growth chamber studies (5,6) legumes responded favorably to the addition of 10% leonardite while grass production was decreased. Trace element sorption by these materials was possible cause for this differential response. In an initial study (2) the sorption and subsequent extractability of Fe^{+3} , Al^{+3} , Cu^{+2} , Zn^{+2} and Mn^{+2} by water, hydrochloric acid, ammonium acetate, DTPA-TEA and EDTA were determined, as was phosphorus sorption by the trace element saturated leonardites. In a second study, preliminary results of which shall be reported here the sorption capacities of 6 lignite materials (3 leonardites and 3 slack coals) were investigated. The materials were quite different in terms of humic acid content, total cations and sorption capacity. Leonardite is generally considered to be a lignite which is oxidized in situ, whereas slack coal is the upper layer of exposed coal seams and is not as highly oxidized.

The methods and results of the two experiments will be treated separately, but since the experiments are closely related they will be discussed together.

EXPERIMENT I

Methods and Materials

A 60-gm sample of "Enderlin leonardite" (obtained from Prairie States Fertilizer Co.) was placed in a buchner funnel and successive aliquots (100 ml, 100 ml, 150 ml) of 0.1N solutions of Fe^{+3} , Al^{+3} , Cu^{+2} , Zn^{+2} or Mn^{+2} (all adjusted to pH 2) were passed through the sample and collected by suction filtration. The samples were then washed with 3-100 ml aliquots of distilled-deionized water, and dried. Replicated 4-gm samples of each of the five "saturated leonardites" and an untreated control were extracted by shaking for 2 hours with 20 ml of each of five extractants (water, 1N ammonium acetate, 0.005 M DTPA-TEA and 0.02 M EDTA). Samples of each saturated leonardite and control were then digested with 5:1, nitric: perchloric acids to determine whether there were changes in elemental composition due to cation exchange by the saturating ion and solution of soluble components. Cation concentrations were determined by atomic absorption spectrophotometry.

Since several studies have shown possible interactions between phosphorus and leonardite (1,4) samples (4-gm) of each saturated leonardite were also treated with 40 ml of 500 and 1000 ppm phosphorus (as $\text{Ca}(\text{H}_2\text{PO}_4)_2$). After 3 days the P remaining in solution was determined by the molybdophosphoric blue color method (3).

Results

It was found that Fe^{+3} had the highest sorption (56 me/100 g) followed in decreasing order by Cu^{+2} , Al^{+3} , Zn^{+2} and Mn^{+2} (53, 51, 45 and 35 me/100 g, respectively). These results agree with the studies of fulvic acid extracted from Podzol Bh horizons by Schnitzer (7) in which the stability constants of several cations with the fulvic acid decreased in the following order at pH 3.5: Fe^{+3} , Al^{+3} , Cu^{+2} , Fe^{+2} , Ni^{+2} , Pb^{+2} , Co^{+2} , Ca^{+2} , Zn^{+2} , Mn^{+2} , Mg^{+2} .

The major cations in the untreated control samples were Ca^{+2} , Al^{+3} , Fe^{+3} , Mg^{+2} , and Na^{+1} ; the remaining cations contributed less than 1 me/100 g (Table 2). The total cation content was higher in all samples that had been saturated by any trace element than in control samples. The major and minor cations behaved differently in the saturation process. Calcium⁺², Mg⁺², Na⁺¹ were higher in the control than in the saturated samples. The decrease was presumed to be primarily a result of solution of soluble salts. The average quantity of Ca^{+2} , Mg^{+2} , and Na^{+1} remaining (non-replaceable) after saturations ranged from about 5% to 40% of the control concentrations (Fig. 1). Iron and Al had the highest sorption and appeared to be most tightly bound, however, the control samples and those saturated by any other cation were nearly equal. Consequently the replaceable fraction is very low (Fig. 1). The minor components appeared to behave similarly, all were low in the control and decreased by about 50% in the saturated samples.

The water, HCl and ammonium acetate extractions of saturated samples indicate that Fe^{+3} is most tightly bound, followed by Al^{+3} , Cu^{+2} , Zn^{+2} and Mn^{+2} . Since EDTA, a relatively strong chelating agent, removed about 50% of each cation, it is probable that the complexes formed have a stability similar to EDTA-cation complexes (Fig. 2).

Phosphorus sorption was highest (more than 90% of added P) in those samples which were saturated by Fe^{+3} and Al^{+3} . Samples saturated with Cu^{+2} , Zn^{+2} and Mn^{+2} sorbed amounts similar to that of the control.

EXPERIMENT 2

Methods and Materials

Origin and humic acid content of the lignitic materials used in this study were as follows:

SYMBOL	CLASSIFICATION	HUMIC ACID CONTENT %	ORIGIN
GPY	Leonardite	89.27	Gascoyne mine, Adams Co., ND
RR	Leonardite	85.76	Gascoyne mine, Adams Co., ND
E	Leonardite	65.29	Prairie States Fert. Co., Ransom Co., ND ¹
SB	Slack Coal	2.35	South Beulah Mine, Mercer Co., ND
GH	Slack Coal	2.84	Glenharold Mine, Mercer Co., ND
PYR ²	Slack Coal	11.91	South Beulah Mine, Mercer Co., ND

¹Mined at undisclosed location in Adams Co., ND

²Contains pyritic inclusions.

Each of the above materials was saturated with 0.1 N salts of Fe^{+3} , Al^{+3} , Cu^{+2} , Zn^{+2} , Mn^{+2} (adjusted to pH 2) by shaking a 2-g sample with two successive 20 ml aliquots of the solution. After shaking for 2 hours they were allowed to stand overnight, centrifuged and the supernatant decanted. The samples were then washed with two 30 ml-water rinses and dried at 80°C for storage.

Samples (100 mg) for total analysis were digested in 3 ml of 1:5 nitric: perchloric acid, made up to 50 ml volume, and filtered. Cation concentrations were determined with Perkin-Elmer Models 403 and 503 atomic absorption spectrophotometers using standard instrument methods.

Results

The sorption was determined by analysis of both the quantity lost from the saturating solution and by the difference between the content of the control and saturated samples. In general the estimates based on the total analysis gave higher sorption, and the correlation was highly significant ($r=0.93$) (Fig. 3). The GPY sample had the greatest sorption capacity followed in decreasing order by SB, GH, RR, E and PYR (Fig. 4). As in the first experiment, Fe^{+3} , Al^{+3} and Cu^{+2} had the highest sorptions for all samples followed by Zn^{+2} and Mn^{+2} (Fig. 4 and Table 1).

Table 1. Sorption of trace elements by lignitic materials, based on the difference between total content of saturated and control samples.

Source	Fe	Al	Cu	Zn	Mn
	Sorption, me/100 g				
GPY	189.1	251.3	175.6	130.9	123.4
SB	137.8	117.9	117.4	91.8	110.6
GH	87.0	84.5	96.0	68.2	39.3
RR	111.2	97.8	96.0	47.4	35.3
E	107.4	77.8	81.8	35.2	24.7
PYR	97.8	66.7	63.0	35.2	18.3

The Fe^{+3} , Al^{+3} or Cu^{+2} concentrations of samples saturated by any other cation (e.g. Fe^{+3} in Al^{+3} , Cu^{+3} , Mn^{+2} or Zn^{+2} saturated samples) were similar to those of the control (Table 2) for all the materials tested. Zinc was significantly decreased in the saturated SB and PYR samples, and Mn was decreased by 50 to 90 percent in the saturated RR, E and PYR samples as compared to control. Sodium loss was almost uniform regardless of the saturating ion (Table 3) and appears to be lost roughly in proportion to the quantity originally present. Calcium and magnesium loss during saturation was greatest for Fe^{+3} and Al^{+3} saturations, commonly resulting in decrease of more than 90% regardless of the material. Manganese, Zn^{+2} and Cu^{+2} saturation allowed about 30-40 me/100 g more Ca and about 1-5 me/100 g more Mg to be retained by the materials.

Discussion and Conclusions

These materials are probably very similar in their behavior to naturally occurring humic materials since their sorption of Fe^{+3} , Al^{+3} , Cu^{+2} , Zn^{+2} , Mn^{+2} shows no serious conflict with the stability constants for fulvic acid cation complexes. However, there is not a good correlation between the humic acid content as determined by alkali extraction and trace element sorption. This may be an indication of the formation of complexes with compounds very different than humic acids. Further research is needed to determine the active functional groups and their bonding mechanisms. Results of the EDTA extraction in the first experiment indicate that at least for the "Enderlin" leonardite the major mechanism is probably chelation.

Before these materials are used as amendments for soils deficient in organic matter they should be tested for humic acid content, Fe^{+3} and Al^{+3} sorption and Na^{+1} , Ca^{+2} and Mg concentrations. The ideal material should have high humate and low Fe^{+3} and Al^{+3} sorption, which as a consequence will result in less P fixation. Since in this study it was found that Na^{+1} , Ca^{+2} and Mg^{+2} were easily lost they may potentially add to existing salinity or sodicity problems. In addition the Ca^{+2}

released may further fix phosphorus in marginally deficient systems. Of the materials tested the RR sample fits these criteria best and holds the greatest promise. A growth chamber study to test its effect on plant growth is planned.

Table 2. Concentration of major elements and trace elements in digested control samples.

Sample	Ca	Mg	Na	Fe	Al	Cu	Zn	Mn
	me /100 g				ppm			
GPY	197.5	120.8	18.3	43.0	70.0	43	25	93
SB	142.5	52.5	7.0	115.5	86.7	60	113	250
GH	110.0	45.8	58.7	31.1	36.7	33	38	55
RR	225.0	58.3	15.7	56.4	44.5	33	18	175
E	137.5	58.3	8.7	55.3	70.0	28	33	300
PYR	66.5	41.7	39.1	88.6	55.6	110	130	140

Table 3. Comparison of quantity of Ca, Mg and Na removed by saturating cations.

		Saturating Cation				
		Fe	Al	Cu	Zn	Mn
Calcium me /100 g	GPY	182.7	185.6	136.3	91.3	106.8
	SB	140.8	141.2	136.7	107.5	105.3
	GH	101.9	103.3	99.8	77.5	82.0
	RR	207.6	218.6	203.8	183.8	198.0
	E	122.0	130.0	116.7	107.5	107.3
	PYR	65.4	65.1	64.2	63.2	65.8
Magnesium me /100 g	GPY	118.2	112.7	109.8	99.6	96.5
	SB	36.2	38.4	36.4	34.6	32.4
	GH	31.8	38.3	41.2	38.5	38.5
	RR	57.0	56.5	56.4	54.9	55.1
	E	56.8	55.4	56.3	59.4	55.7
	PYR	35.8	35.8	34.5	33.8	30.0
Sodium me /100 g	GPY	11.9	11.8	11.4	11.7	13.7
	SB	--	--	--	--	--
	GH	51.6	50.2	50.9	50.9	52.2
	RR	9.6	9.9	9.1	9.0	12.8
	E	2.6	2.0	2.2	2.5	3.6
	PYR	32.3	32.2	31.6	32.6	34.9

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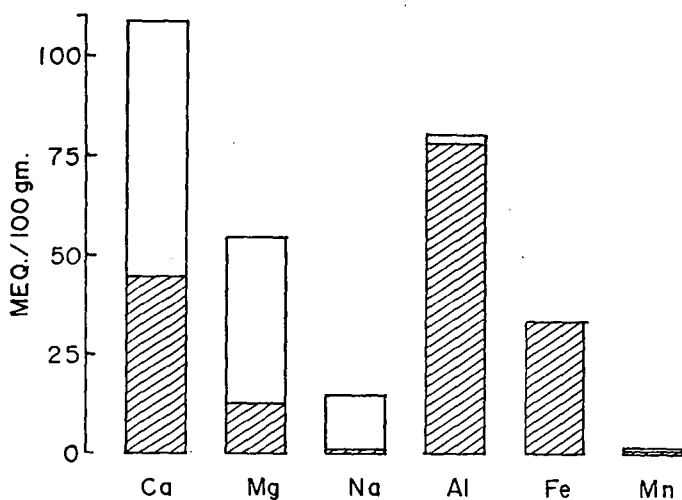


Fig. 1 Total and non-replaceable (shaded) concentrations of the dominant cations and manganese in E leonardite.

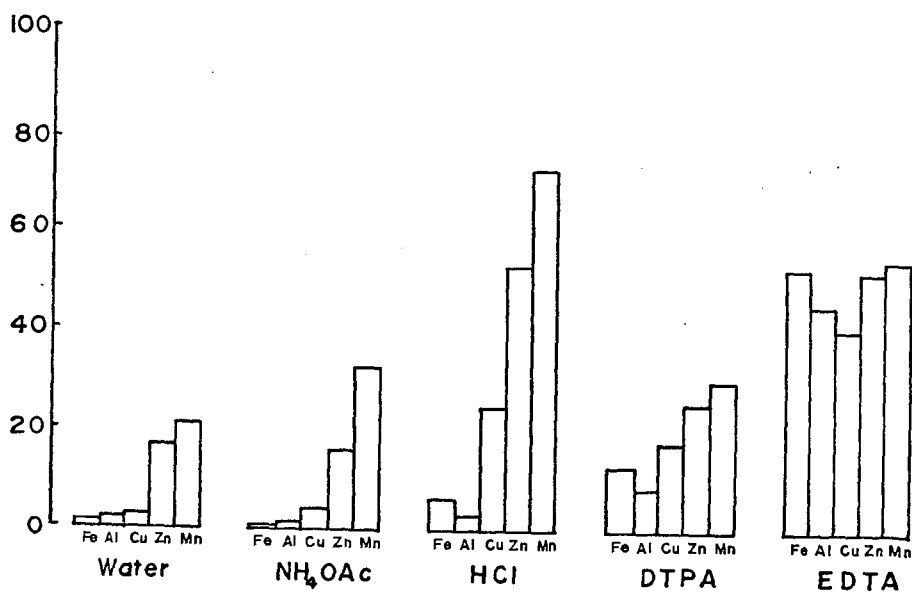
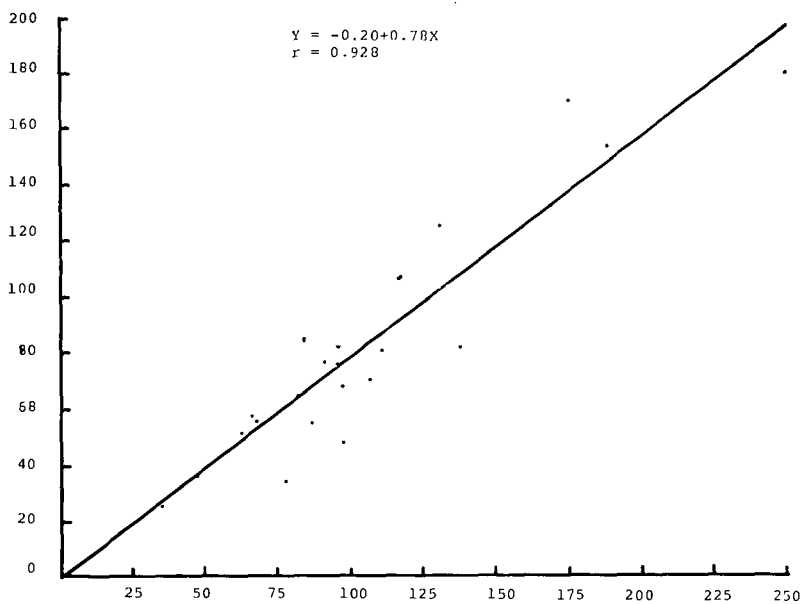


Fig. 2 Percentage of the sorbed cation that was extractable by several extracting solutions.

Sorption, me/100 g, by quantity retained in saturating solution



Sorption, me/100 g, by difference between saturated and control samples (acid digestion)

Figure 3. Comparison of sorption estimates by two methods.

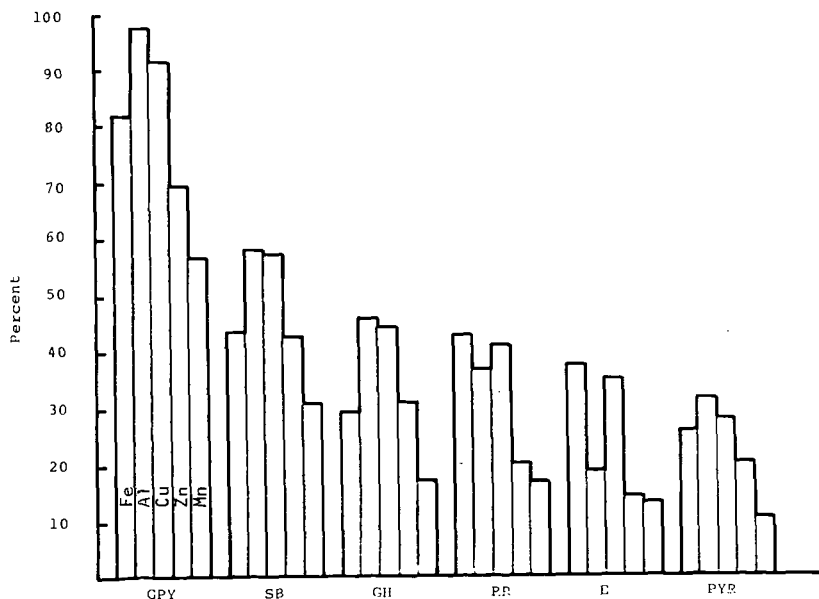


Figure 4. Quantity of trace element sorbed, as estimated by loss from the saturating solution, expressed as a percent of the total added.